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Effects of hydrogenation on interlayer reactions in metallic multilayers

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Abstract

The effects of dissolved hydrogen on the evolution and kinetics of interlayer reactions in polycrystalline Ni/Mg multilayer and Ni/Nb bilayer have been investigated by X-ray diffraction and Auger electron depth profiling. In the Ni/Mg multilayer, the reaction producing Mg_2Ni or β-Mg_2NiH_4 is retarded by hydrogenation at $\lesssim$373 K, whereas at $\gtrsim$473 K it little influences the reaction rate. This is in contrast with Ni/Ti and Pd/Ti multilayers studied previously, where the interlayer reactions are completely suppressed by hydrogenation. On the other hand, in the Ni/Nb bilayer, the reaction producing Ni_3Nb is greatly enhanced by hydrogenation at $\gtrsim$723 K compared with that without hydrogen which takes place only at $\gtrsim$798 K. This enhanced reaction by hydrogenation may be related with superabundant thermal vacancies coexisting with dissolved hydrogen atoms in the Nb layer. The asymmetrical growth of Ni_3Nb toward the Nb layer is reasonably explained by the enhanced interdiffusion in this layer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ni/Mg multilayer; Ni/Nb bilayer; Interlayer reaction; Interdiffusion; Hydrogenation; X-ray diffraction; AES depth profiling

1. Introduction

The interphase reaction in a metallic alloy is more or less influenced by the presence of dissolved hydrogen. Hydrogen may retard or inhibit the reaction either by forming a stable hydride with one of the constituents of the alloy and suppressing the interdiffusion in the alloy, or by decomposing the reaction product (a compound) into a mixture of another compound and a stable hydride (disproportionation). Conversely, it may enhance the reaction by assisting the interdiffusion in the alloy. These effects of hydrogen on the interphase reaction can be simulated by observing the interlayer reaction in a metallic multilayer or bilayer under hydrogen atmosphere.

We have recently studied interlayer reactions in Ni/Ti [1,2], Pd/Ti [1,3,4] and Fe/Ti [5] polycrystalline multilayers subjected to annealing in vacuum and hydrogen atmosphere at elevated temperatures, and found that in all these systems the interlayer reaction readily took place during annealing in vacuum forming amorphous alloys (Ni/Ti, Pd/Ti) or an intermetallic compound (Fe/Ti), whereas it was *almost completely suppressed* under hydrogen because the Ti layers were instantaneously transformed to TiH_2 which strongly inhibited the interlayer reaction. These results are briefly summarized in Table 1.

In the present work, the Ni/Mg and Ni/Nb systems are studied in a similar manner as above. It will be shown that, in polycrystalline Ni/Mg multilayers, the interlayer reaction is *slightly suppressed* or *unaffected* by the hydrogenation depending on temperature, while, in polycrystalline Ni/Nb multilayers, the reaction is *greatly enhanced* by the hydrogenation. These different effects of dissolved hydrogen on the interlayer reactions in metallic multilayers are discussed.

2. Experimental procedure

Multilayer and bilayer films of Ni/Mg and Ni/Nb systems with various layer thicknesses were deposited on Si(111) substrates with Ar-ion-beam sputtering technique at ambient temperatures. The period of the multilayer was controlled by choosing an appropriate sputtering time for each metal target with a specific sputtering rate. It was precisely determined by analysing low-angle X-ray diffraction peaks from the artificial periodic lattice of the film. The interlayer reaction in the multilayer or bilayer was caused by annealing in vacuum (8×10^{-5}Pa) or hydrogen atmosphere (0.5 MPa H_2) of 99.9999% purity at elevated temperatures. The phases formed in the films were identified by X-ray diffraction (XRD) with Cu Kα radiation at room temperature in a symmetrical reflection mode (S-mode; $\theta/2\theta$ scan) or a grazing-incidence mode (G-mode; 2θ scan) with an incidence angle of 2°. The variation of

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Table 1
Behavior of metallic multilayers or bilayer subjected to annealing in vacuum or hydrogen atmosphere

Sample (net composition)	Annealing condition	Reaction products and characteristics		Ref.
		Annealed in vacuum	Annealed in H_2 (0.5 MPa)	
Ni/Ti multilayer ($Ni_{44}Ti_{56}$)	523 K 86.4 ks	Ni–Ti amorphous alloy Homogenized by interdiffusion	Ni/TiH_2 multilayer Interlayer mixing is inhibited	[1,2]
Pd/Ti multilayer ($Pd_{38}Ti_{62}$)	623 K 86.4 ks	Pd–Ti amorphous alloy Homogenized by interdiffusion	Pd/TiH_2 multilayer Interlayer mixing is inhibited	[1,3,4]
Fe/Ti multilayer ($Fe_{60}Ti_{40}$)	523–823 K 10.8–108 ks	FeTi+(Fe)[a] Homogenized by interdiffusion	Fe/TiH_2 multilayer Interlayer mixing is inhibited	[5]
Ni/Mg multilayer ($Ni_{34}Mg_{66}$)	323–573 K 10.8–108 ks	Mg_2Ni+($MgNi_2$)[a] Homogenized by interdiffusion	β- or β′-Mg_2NiH_4+($MgNi_2$)[a] Homogenized by interdiffusion at $\gtrsim$473 K, but retarded at $\lesssim$ 373 K	This work
Ni/Nb bilayer ($Ni_{63}Nb_{37}$)	523–823 K 10.8–108 ks	Ni_3Nb+(Nb)[a] Homogenized by interdiffusion at $\gtrsim$798 K	Ni_3Nb+(Nb)[a] Homogenized by enhanced interdiffusion at $\gtrsim$723 K	This work

[a] Parenthesis means a minor fraction.

concentration modulation due to the reaction in the multilayer or bilayer was measured with Auger electron spectroscopy depth profiling (AESDP). Details of the technique and data analysis of the AESDP are given elsewhere [1,4].

3. Results

3.1. Ni/Mg multilayer

A multilayered film of [Ni(6 nm)/Mg(24 nm)]$_{10}$/Si(111) with a net composition of $Ni_{34}Mg_{66}$ was prepared. The designed period of the multilayer $\Lambda = 30$ nm was consistent with the observed value of 29.1 nm obtained from low-angle XRD peaks of the artificial lattice. Fig. 1a,b shows XRD patterns of the film subjected to annealing in vacuum at temperatures between RT and 573 K for 108 ks (30 h) measured in the S-mode and G-mode, respectively. In the S-mode, crystallite planes parallel to the film plane contribute to the diffraction, while in the G-mode, those nonparallel to it can be detected. As shown in the S-mode, the as-deposited film consists of a stacking of layers preferentially oriented for Ni(111) and Mg(001) with no interlayer alloy phases. Upon annealing at 323 K, the formation of Mg_2Ni is slightly indicated, and it rapidly grows at the expense of Ni and Mg layers up to 473 K; finally, at 573 K, the film is totally composed of the equilibrium phases of Mg_2Ni and $MgNi_2$. This annealing behavior of the multilayer can also be recognized for the G-mode, where the signals from the constituent Ni and Mg layers are relatively diminished and those from the reaction products are enhanced.

Fig. 2a,b shows similar XRD results on the same multilayered film subjected to annealing under 0.5 MPa H_2. Combining the results of S- and G-modes, it can be recognized that the Mg layer is partly hydrided to form MgH_2 between RT and 373 K, where a sign of the formation of β hydride (low-temperature phase of Mg_2NiH_4) is also indicated. At 473 K the film is mainly composed of the β-hydride with a slight residual Ni, while at 573 K they are transformed to the equilibrium phases of β′-hydride (high-temperature phase of Mg_2NiH_4) and $MgNi_2$. On the basis of Figs. 1 and 2, it can be concluded that the hydrogenation of the Ni/Mg multilayer causes no significant influences on the evolution and kinetics of the interlayer reaction except that the reaction is slightly retarded in the temperature range between 323 and 473 K and that Mg_2NiH_4 (β or β′) is formed instead of Mg_2Ni.

Fig. 3a,b shows AESDP results of the Ni/Mg multilayer subjected to annealing in vacuum and hydrogen atmosphere, respectively, where the concentration modulations of Ni and Mg along the depth of the film are displayed. In most of the profiles, the modulation amplitude tends to decay with increasing depth from the surface down to the substrate. This decay does not represent a true feature of the concentration variation but an experimental artifact due to ion mixing and surface roughening during sputtering in the AESDP process; thus, only the first a few periods provide the true feature of the modulation. The concentration modulation of the as-deposited film is rapidly smoothed out for annealing in vacuum at 373 and 473 K. On the other hand, for annealing in H_2 atmosphere, it is less rapidly smoothed out at 373 K; however, it is almost homogenized at 473 K like that after annealing in vacuum. The smoothing of the concentration modulation is caused by interlayer reactions, and these results are consistent with those of XRD.

3.2. Ni/Nb bilayer

A bilayered film of [Ni(100 nm)/Nb(100 nm)]/Si(111) with a net composition of $Ni_{63}Nb_{37}$ was prepared for studying the influence of hydrogenation on the interlayer reaction process and kinetics in the Ni/Nb system. The film was subjected to annealing in vacuum or 0.5 MPa H_2 atmosphere at temperatures between 523 and 823 K for

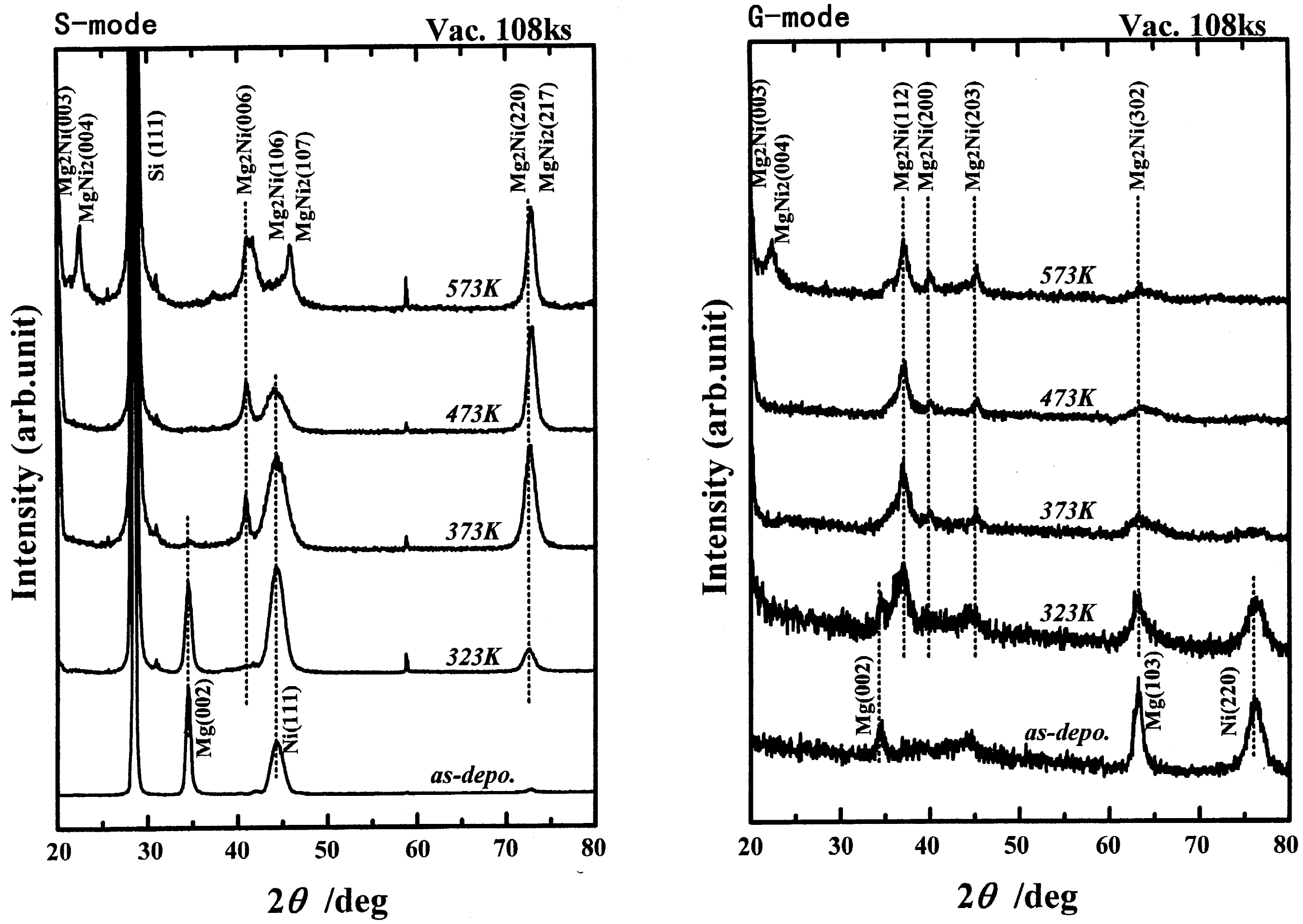

Fig. 1. (a,b) XRD patterns of the Ni/Mg multilayer subjected to annealing in vacuum for 108 ks, measured in the S-mode and G-mode, respectively.

10.8 ks (3 h). The phases formed and the change in composition along the depth of the film associated with the reaction were examined by XRD and AESDP, respectively.

Fig. 4a,b shows XRD patterns measured in the S-mode of the Ni/Nb bilayer subjected to annealing in vacuum and hydrogen atmosphere, respectively. In the as-deposited film, preferentially oriented Ni(111) and Nb(110) peaks are seen. Annealing in vacuum causes no significant changes of these peaks up to 773 K except for an upward shift of the Nb(110) peak due to recovery of planar internal stress. Upon annealing at 798 K, Ni_3Nb(020) peak appears at the expense of Ni(111) and Nb (110) peaks. On the other hand, annealing in hydrogen atmosphere causes the Ni_3Nb(020) peak to appear at 723 K and increase up to 823 K at the expense of Ni(111) and NbH_x(111) peaks. The latter peak appears because bcc Nb dissolving hydrogen is transformed to a fcc hydride NbH_x at RT. These XRD results indicate that the interlayer reaction forming Ni_3Nb is substantially enhanced by the hydrogenation at and above 723 K, where plenty of hydrogen is dissolved in the bcc Nb layers.

Fig. 5 shows AESDP results of the Ni/Nb bilayer subjected to annealing in vacuum and H_2 atmosphere for 10.8 ks at temperatures between 523 and 823 K, compared with that of the as-deposited one. It can be clearly seen that, for annealing in vacuum, the bilayer structure is nearly kept up to 773 K, while at 798 K, Ni_3Nb suddenly emerges at the interface and continues to grow in both directions nearly symmetrically. The formation of Ni_3Nb can be inferred from the relative composition of Ni to Nb. The reason for a compositional anomaly seen at the original interface in this sample is not clear, but it may be due to segregation of oxygen impurities to the interface. On the other hand, for annealing in H_2 atmosphere, the formation and growth of Ni_3Nb take place at temperature as low as 723 K, and furthermore, the growth rate is much faster toward the Nb layer than the Ni layer. These features are consistent with those found in the XRD study. In this system, the interlayer reaction is significantly enhanced by the presence of dissolved hydrogen. The asymmetrical growth of the Ni_3Nb phase toward the Nb layer is a characteristic effect of the hydrogen-enhanced reaction in this system. This enhancement has also been found for a Ni/Nb multilayer (not shown). The anomaly developing at

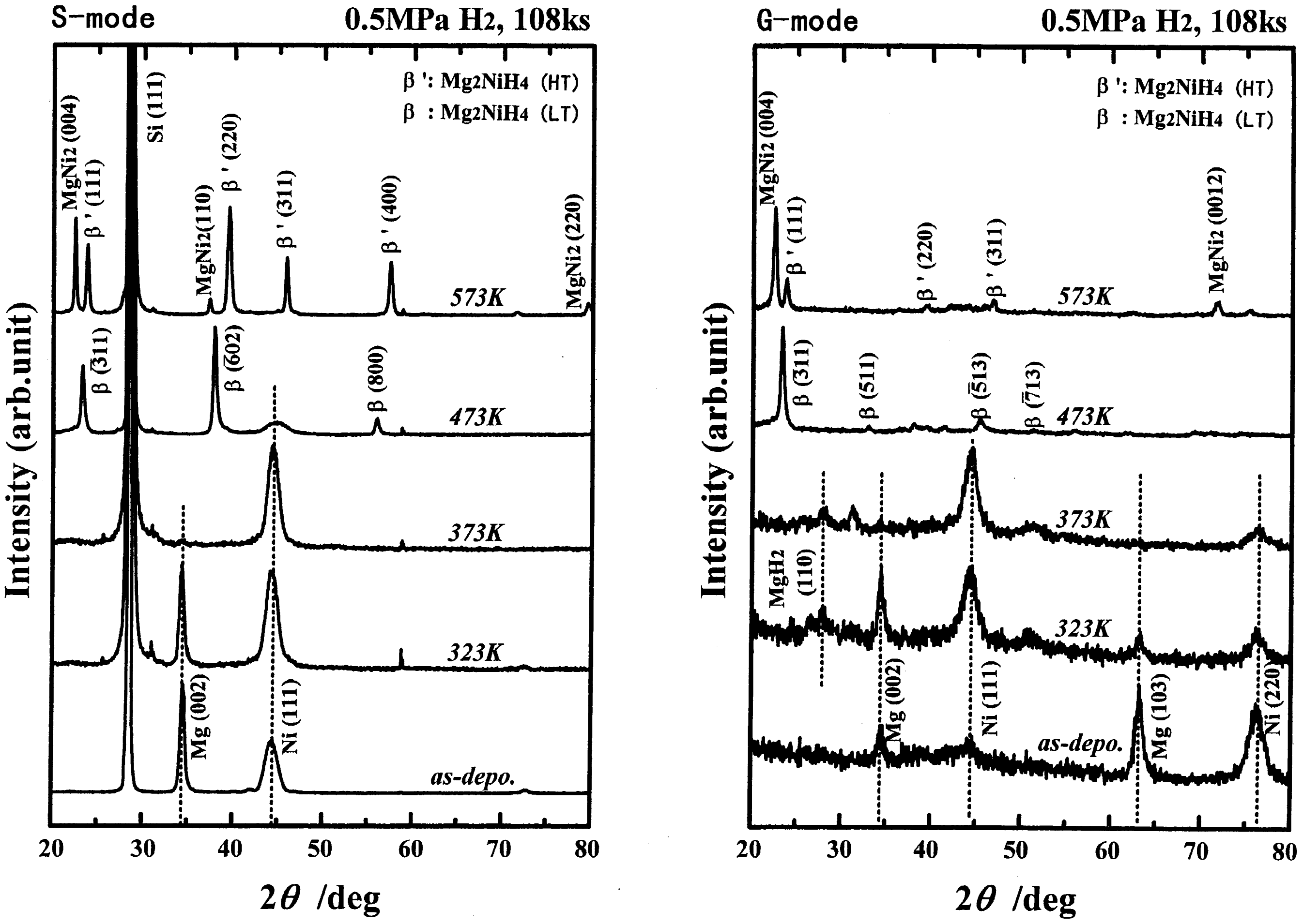

Fig. 2. (a,b) XRD patterns of the Ni/Mg multilayer subjected to annealing in 0.5 MPa H_2 atmosphere for 108 ks, measured in the S-mode and G-mode, respectively.

the surface of the film with increasing temperature is due to selective oxidation of Nb to form NbO_2. Since the interlayer reaction is taking place well below the surface of the film, the oxidation does not significantly influence the reaction if the temperature is kept below 823 K.

4. Discussion and conclusions

In the Ni/Mg multilayer, the interlayer reaction takes place above 323 K and the films become nearly homogenized forming Mg_2Ni above 473 K in vacuum. Hydrogenation of the multilayer somewhat retards the interlayer reaction around 323–373 K, but it causes no significant effect on the reaction kinetics above 473 K, forming β-Mg_2NiH_4 nearly uniformly over the film. This may be thermodynamically explained as follows [6]: At lower temperatures under 0.5 MPa H_2, the net change in Gibbs-free energy, ΔG, for a reaction $2MgH_2+Ni \rightarrow Mg_2Ni+2H_2 \rightarrow \beta\text{-}Mg_2NiH_4$ is positive ($\Delta G>0$) and the reaction is forbidden, whereas, at higher temperatures, $\Delta G \leq 0$ and the reaction is allowed. The critical temperature should depend on the hydrogen pressure. To substantiate this, however, an inhibition of this reaction under higher hydrogen pressures at temperatures above 373 K must be confirmed.

On the other hand, in the Ni/Nb bilayer, the interlayer reaction forming Ni_3Nb is initiated at 798 K in vacuum, whereas it occurs even at 723 K under hydrogen. The enhancement of the reaction by hydrogenation may be caused by superabundant thermal vacancies present in the Nb layer together with dissolved hydrogen atoms, which greatly assist the interdiffusion in the bilayer [7]. The asymmetrical growth can be reasonably explained in terms of this mechanism.

The present results provide us with new aspects of hydrogen effects on the interlayer reactions in metallic multilayers or bilayers, as shown in Table 1. Effects of hydrogen on structures and properties of interfaces in metallic multilayers or bilayers have been studied by several researchers [8–11]. However, most of them are not concerned with the structural stability or instability of the films caused by the hydrogenation. Our study as summarized in Table 1 may be the first one reported up to present in this field.

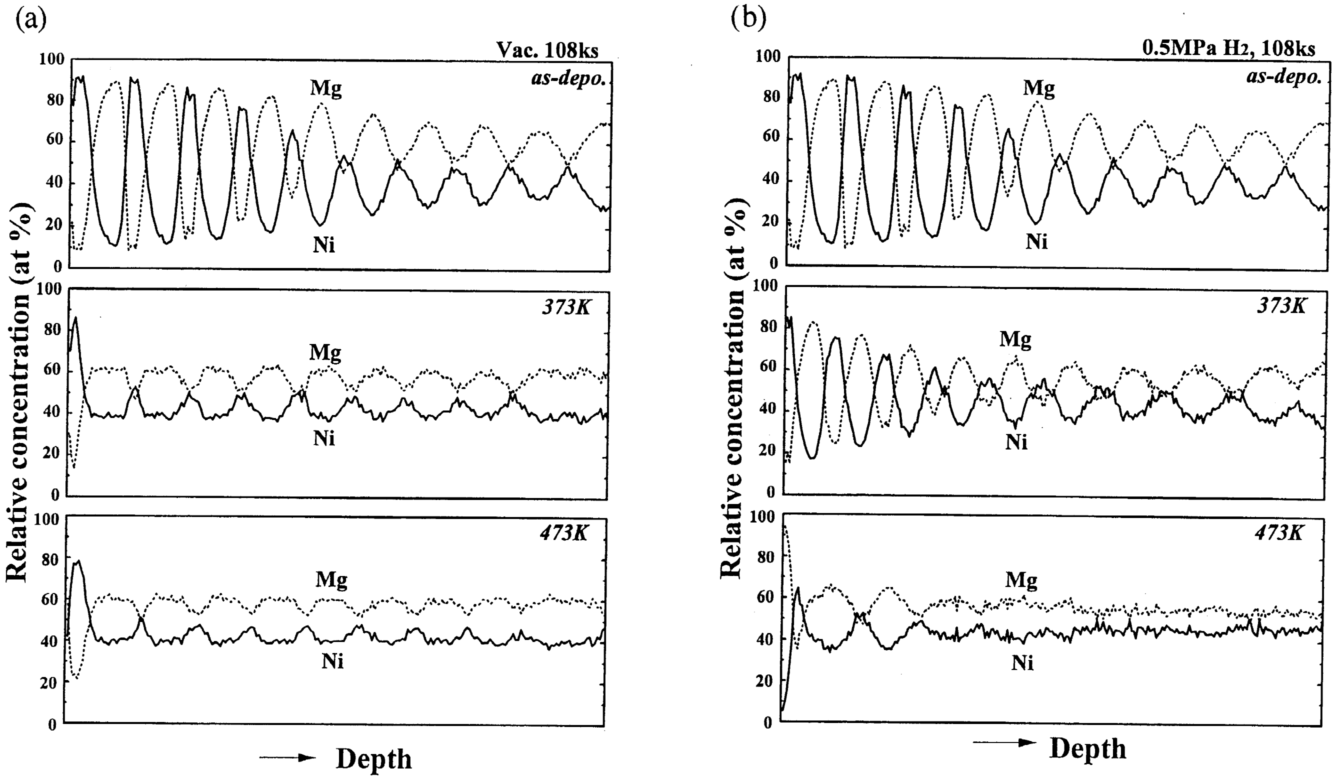

Fig. 3. (a,b) AESDP patterns of the Ni/Mg multilayer subjected to annealing in vacuum and 0.5 MPa H_2 atmosphere, respectively, for 108 ks at indicated temperatures.

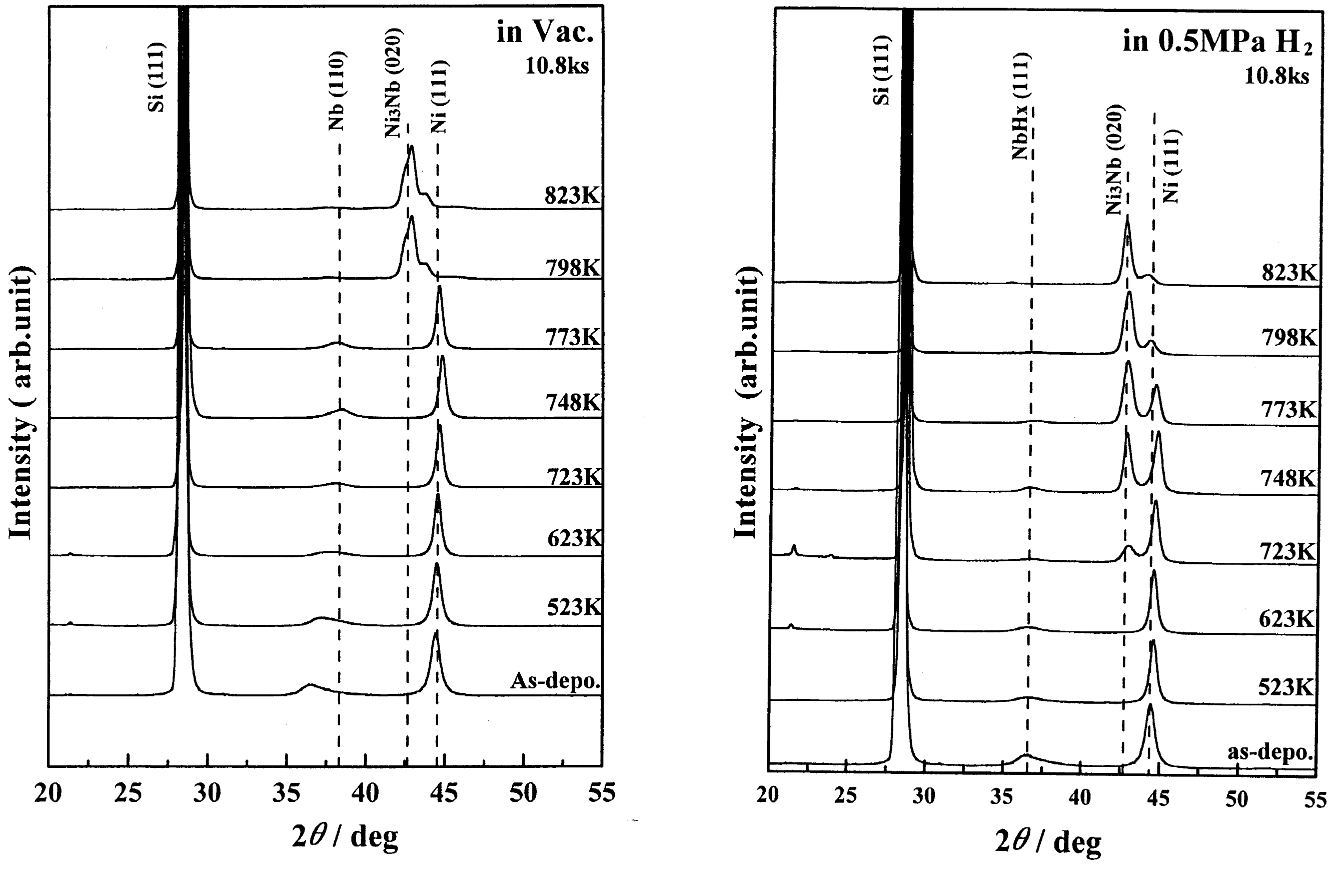

Fig. 4. (a,b) XRD patterns of the Ni/Nb bilayer subjected to annealing in vacuum and 0.5 MPa H_2 atmosphere, respectively, for 10.8 ks measured in the S-mode.

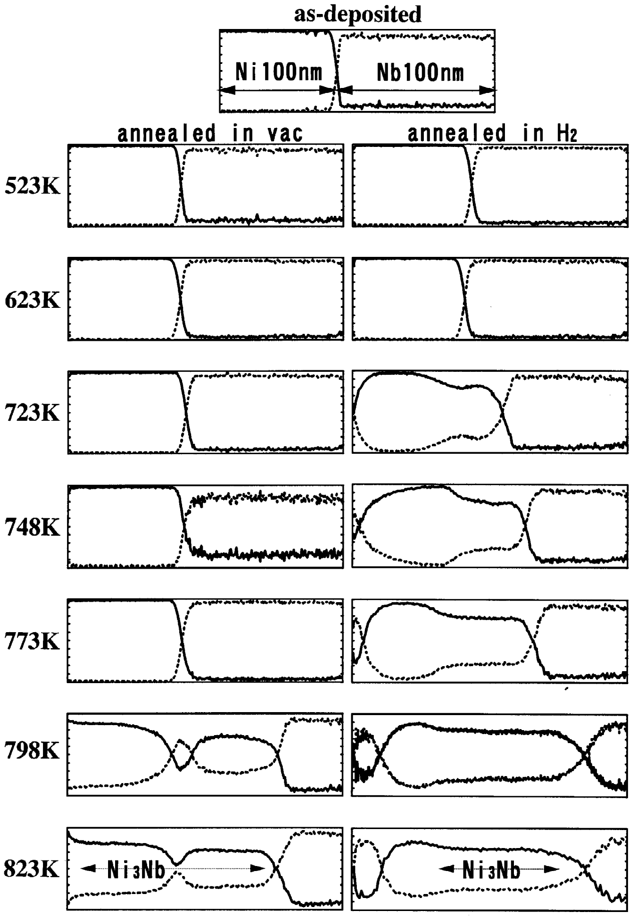

Fig. 5. AESDP patterns of the Ni/Nb bilayer as-deposited and subjected to annealing in vacuum and 0.5 MPa H_2 atmosphere for 10.8 ks at temperatures between 523 and 823 K.

Acknowledgements

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